

## Particle Transport Through Porous Media

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Transport of suspended particulate matter is widely recognized to occur in subsurface environments. Field data indicate that viruses, bacteria, and clay minerals can migrate considerable distances and that small particles and macromolecules are implicated in the transport of organic contaminants and radionuclides. Furthermore, media permeability can be significantly altered by changes in aqueous chemistry through particle release and capture. Quantitative models for predicting particle transport are available within the water filtration literature that account for the mechanisms of particle-media collisions and the conditions for attachment. Predictions from the filtration models are used to analyze particle migration through porous media at typical groundwater flow velocities. As particles accumulate within media pores, available models become less predictive because of the coupling between particle retention and permeability reduction. An examination of filtration data reveals that retention of a relatively small solid volume within media pores can reduce media permeability by orders of magnitude. The fact that contaminants adsorbed to particles are mobile has important implications in understanding and predicting contaminant transport. The design of laboratory experiments and the collection of field samples often neglect contaminants transported by suspended colloids and particles.

### 1. INTRODUCTION

The fate of many pollutants in the aquatic environment is determined by the fate of the particulate matter with which they are associated. The transport and bioavailability of hydrophobic organics and toxic metals, for example, depends on the degree of partitioning of these compounds between solution and solid phases. The solid phase consists of both stationary and mobile, or suspended, states. In some instances, the compounds of interest are particulate to begin with, as is the case with metal sulfide precipitates, bacteria, viruses, and asbestos fibers. In all cases, the suspended particles of most concern with regard to transport potential are in the clay and colloidal size ranges (micrometer and submicrometer). These small particles have high surface areas per unit mass, thus posing a significant sorption potential. Since they are considerably smaller than sands and gravels encountered in groundwater aquifers, migration of compounds associated with the suspended solid phase may occur, a process as yet not adequately considered in predictive models of contaminant migration.

In addition to pollutant transport, small particles in porous media can affect permeability by clogging pores. The use of drilling muds and clay liners for waste isolation are examples of where the clogging effect is desirable and sought. However, permeability reduction during water flooding operations in the petroleum recovery industry or during recharge of aquifers is not desirable and poses a major problem. Thus it is of great importance to understand the migration behavior of particles in porous media as well as delineate factors affecting this migration.

This paper addresses the importance of particle migration through porous media by reviewing literature in subject areas where this is a consideration and by examining methods available to quantify such migration. A discussion of deficiencies in conventional predictive methods for adsorptive contaminant and particulate transport is also provided. In particular, problems with using the distribution coefficient approach to model

partitioning of pollutants between mobile and immobile phases and with determining the pattern of solids accumulation and permeability reduction in porous media are identified.

Prior to commencing the discussion, a brief summary of terminology and concepts used may be helpful. Throughout this review, colloidal materials suspended in water are referred to as particles. Porous media refers to a fixed bed of granular material containing pores through which a solution may flow. Particles that collect on the porous media form a deposit that can alter fluid flow properties and decrease the permeability. Under constant hydraulic head, permeability reduction is measured by a decrease in flow rate. At constant flow rate, permeability reduction is indicated by increased hydraulic gradient.

Figure 1 illustrates three mechanisms that can limit particle migration, and these mechanisms will be used in the following discussion of the literature and of filtration theory. For particles and particle aggregates comparable in size to or larger than the porous media grain size, penetration into the media will not occur, but rather a filter cake or surface mat will form above the media. As a result, substantial particle accumulation can occur, leading to a decrease in permeability. Particles small enough to enter the porous media can be mechanically removed by straining in smaller pore spaces. Particle straining has limited capacity for particle accumulation, and little decrease in permeability is expected. Frequently, straining near the face of porous media further restricts openings, allowing smaller particles and aggregates to be retained in a surface mat.

Very small particles relative to the porous media grain size can be removed from solution by physical and chemical forces between particles and the media. Particles in natural waters and aquifers possess surface charges controlled by surface groups and aqueous chemistry. Electrostatic and London-van der Waals forces determine if particle-media and particle-particle associations are favorable. Particle-media associations can occur with negatively charged particles and positively charged media or vice versa. The capacity of the media to collect oppositely charged particles is relatively low, as particles cannot attach to already deposited particles; thus little



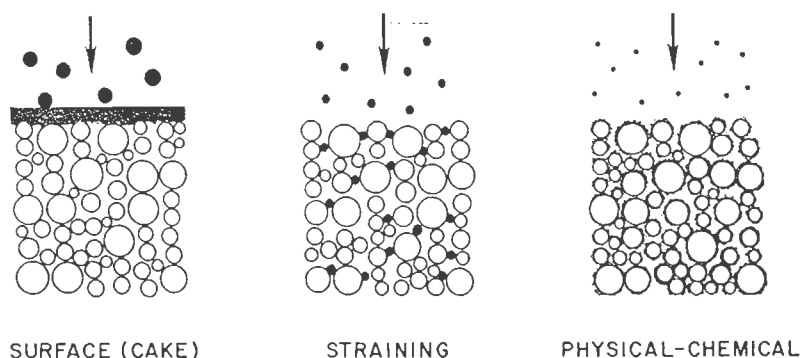


Fig. 1. The three filtration mechanisms generally considered. Note the particle size dependence and difference in deposit morphology.

change in permeability is observed. Changes in aqueous chemistry may destabilize particles so that they flocculate with themselves and attach to media as aggregates via London-van der Waals attractive forces. Destabilization may be accomplished by compression of the diffuse layer of charge surrounding the particles by a high concentration of inert electrolyte; by pH adjustment to the point of zero particle surface charge; or by the presence of counterions that preferentially adsorb onto particles and decrease the net surface charge so that attractive forces dominate. Collection of destabilized particles within porous media can result in a deposit thicker than a monolayer as particle-media and particle-particle attachments occur. The ultimate deposit is controlled by hydrodynamic forces and the strength of the aggregated particles present in the deposit.

## 2. LITERATURE REVIEW

### 2.1. Groundwater Pollution

Besides the ongoing concern of organic solvents and gasoline products found in groundwater, the presence of particulate pollutants indicates further concerns regarding the purity of groundwater. This section considers some instances in which particulate pollutants and particle transported pollutants are implicated in groundwater contamination processes.

**2.1.1. Bacteria and viruses.** Frequently, groundwater is used without treatment because of the perceived filtering action of solution flow through porous media. It is now recognized, however, that bacteria and viruses can travel considerable distances in aquifers and saturated soils, thus posing a contamination threat to surface waters and well waters [Bouwer, 1984]. Recently, a large number of outbreaks of water-borne disease have been attributed to contaminated groundwater [Gerba and Bitton, 1984].

Reviews of pathogen transport through aquifer materials by Gerba *et al.* [1975] and Gerba and Goyal [1985] report bacterial migration from 1 to 830 m and virus migration up to 400 m. Jang *et al.* [1983] demonstrated that some bacteria can travel almost 2 to 4 cm per day in a stagnant nutrient medium within a sandstone core. Wood and Ehrlich [1978] used baker's yeast as a tracer for bacterial movement in a field investigation. Baker's yeast was used as an analogue because of its availability, ease of analysis, and similarity in surface properties to bacteria. They found high mobility of yeast cells and evidence of flow through secondary permeability features or macropores rather than exclusively in intergranular pore spaces. Nonpathogenic bacterial viruses have also been used

as tracers of groundwater and microbial movement for reasons similar to those for yeast [Keswick *et al.*, 1982]. The importance of the soil texture in controlling the mobility of bacteria was investigated by Smith *et al.* [1985]. They determined that 22–79% of the added *E. coli* penetrated 28 cm of various intact soil cores compared to only 0.2–7% penetration through the same depth of sieved and repacked soil. Thus field studies of microbial transport are needed because transport data determined from laboratory and soil columns do not duplicate the actual soil structure in the field.

Field and laboratory studies generally indicate that virus movement through soil is limited predominantly by physical-chemical mechanisms while bacteria, being at least an order of magnitude larger in size, are retained by both physical-chemical mechanisms and straining [Gerba *et al.*, 1975; Corapcioglu and Haridas, 1984]. Straining of bacteria at the soil surface is the "major limitation in their travel through soils," although sedimentation becomes important after the maximum straining capacity has been reached and clusters begin to break away from the clogged region [Gerba and Bitton, 1984, p. 67].

Recent investigations relevant to microbial transport in porous media have focused on factors affecting adsorption of microbes to solids [Lance and Gerba, 1982; Moore *et al.*, 1982; Murray and Parks, 1980; Vilker and Burge, 1980; Vilker *et al.*, 1983], and on the development of models for microbial transport based on adsorption [Vilker, 1981] and sometimes filtration [Cookson, 1970; Corapcioglu and Haridas, 1984]. Adsorption studies have confirmed that clays provide "ideal adsorption sites" for microbes [Gerba and Bitton, 1984], that clay aggregation influences virus adsorption [Vilker *et al.*, 1983], and that adsorption (and desorption) of microbes to (from) solids is highly influenced by aqueous chemistry, the presence of organic compounds including humics, and flow rates [Hagedorn, 1984; Lance and Gerba, 1982; Murray and Parks, 1980].

Rarely are viruses and bacteria present in solution as single particles. Vilker *et al.* [1978] have found in batch adsorption experiments that a very large percentage of added viruses adsorb to wastewater effluent solids. In addition to adsorption to solids, it has been observed that both bacteria and viruses aggregate with themselves, or bioflocculate under many environmental conditions [Costerton *et al.*, 1978; Floyd, 1979; Floyd and Sharp, 1978]. An experiment by Jang *et al.* [1983] involving the injection of bacteria into sandstone cores to determine their rate of transport in such media, demonstrated that aggregating bacteria may clog porous media and hinder



subsequent transport of bacteria. Despite all these indications of the importance of aggregation and adherence to solids, predictive models typically consider only single-particle transport and removal.

**2.1.2. Natural organic matter and hydrophobic organic compounds.** The structure of naturally occurring organic matter in soil and water is generally uncertain, and descriptions ranging from molecular to particulate and aggregate are commonly used [Schnitzer and Khan, 1972]. The presence of a small colloidal (or aggregated) fraction has been demonstrated using small angle X ray scattering measurements of aquatic humic substances [Thurman et al., 1982]. Wershaw and Pinckney [1973] observed that aggregation of humic substances is a function of aqueous chemistry, and they recognized that these aggregates are important in controlling transport through natural waters. Chemical characterization of such organic matter heavily depends on the experimental conditions such as pH, ionic composition, and organic matter concentration. Humic acid aggregation is frequently mentioned to occur during both ultrafiltration [Buffle et al., 1978; Aiken, 1984] and gel filtration chromatography [Barden et al., 1984], altering reported "molecular weight" distributions. Barden et al. [1984] observed that "polymeric acids" obtained from groundwater within oil shale deposits would self-associate or aggregate following dialysis into distilled water. The aggregation was caused by lowering either the pH or the ionic strength. The aggregates were reported to be strong and could only be partially disassociated with detergents. They could not resolve if the "polymeric acids" were themselves distinct molecules or associated aggregates under ambient conditions. Similarly, Merdow et al. [1985] showed that copper binding to fulvic acids induced aggregation as would low pH and high ionic strength conditions.

Self-associated organic molecules may exist as micelles that can strongly influence the transport of contaminants. Wershaw et al. [1969] showed that the presence of 0.5% by weight sodium humate could increase the solubility of DDT by a factor of 20 over that measured in water alone. The sodium humate was referred to as being present as micelles similar to those formed by surfactants. Chiou et al. [1986] observed solubility enhancement of DDT and some PBCs by dissolved humic and fulvic acids. They believe the association is of the partition rather than adsorption type, thus implicating a micellar type of solubilization. Carter and Suffet [1982] also observed the "solubilization" effect of humic acids on DDT but referred to it as an "association" process, due to the uncertainties as to the relative importance of solubilization and sorption processes. The formation of micelles from surfactant solutions has been found to increase the apparent solubility of gases in solution. For surfactant concentrations less than the critical micelle concentration, Bolden et al. [1983] found gas solubilities equaled their solubility in pure water. Once the critical micelle concentration was exceeded, enhanced gas solubility was observed. In experiments conducted with 10% by weight humic acid, Callaway et al. [1984] observed that the vapor pressure of low molecular weight halocarbons was reduced by 20–70%, possibly by the partitioning of the compounds into humic acid micelles.

While micelle formation occurs in surfactant-water solutions once the critical concentration is reached, the presence of particle surfaces can result in surfactant adsorption and hemimicelle formation. As the charged (polar) groups of surfactant

molecules adsorb onto an oppositely charged surface, the hydrocarbon (nonpolar, hydrophobic) end groups can associate into an energetically favorable hemimicelle by excluding water. Fuerstenau et al. [1964], Somasundaran and Fuerstenau [1966], and Wakamatsu and Fuerstenau [1968] have shown that this happens for alkyl sulfonates and that the critical hemimicelle concentration depends inversely on hydrocarbon chain length. The aqueous concentration required for hemimicelle formation is approximately 2 orders of magnitude lower than the critical micelle concentration [Gaudin and Fuerstenau, 1955].

The surfactant nature of naturally occurring organic matter suggests that micelle and hemimicelle formation are possibilities. In studies by Chiou et al. [1983, 1984] on nonionic organic compound partitioning between soil organic matter and water, the analysis and supporting interpretation of experimental data were based on a partitioning of solutes between an aqueous solvent and a humic, polymeric solvent. This suggests that the humic material exists as a separate phase present either as a micelle in solution or as a hemimicelle associated with a solid surface. The distinction between molecular and particulate properties of natural organic matter is uncertain, however. Breger [1970] has suggested that the behavior of 90% of the organic matter in natural waters is determined by colloidal rather than molecular properties. By colloidal phenomena, Breger includes swelling, precipitation, adsorption, flocculation, and micelle formation.

The addition of surfactants to soil-water systems has been shown to alter pesticide mobilities in laboratory and field studies. According to Singhal and Bansal [1978], surfactants may enhance the mobility of pesticides if concentrations are low enough to preclude micelle formation. At higher surfactant concentrations, when micelles are presumably formed, pesticide mobilities are reduced. Lichtenstein et al. [1967] found that surfactants decreased the leachability of parathion present in a soil column, but they did not suggest a mechanism for the increased persistence.

The approach commonly used to model the fate of pesticides and other hydrophobic organic compounds is based on equilibrium partitioning between a mobile dissolved phase and a presumed immobile organic phase. Karickhoff et al. [1979] discussed how batch adsorption experiments could give distribution coefficients that would allow prediction of contaminant migration, lessened by adsorption. However, measured values of distribution coefficients have been found to be inversely related to the concentration of the sorbing solid phase [O'Connor and Connolly, 1980], suggesting that phase separations (i.e., sorbed versus nonsorbed) might not be complete in batch adsorption experiments. Carter and Suffet [1982] noted this phenomenon in their experiments with DDT and humic acids and came to similar conclusions. Karickhoff [1984], in a review of organic pollutant sorption in aquatic systems, also recognizes the possibility of "colloid interference" in determining distribution coefficients. Gschwend and Wu [1985] have demonstrated that nonsettleable particulate matter increases with solids concentration, thus providing a variable and often undetected sorbed phase for a compound. They propose a three-phase equilibration process to account for a dissolved phase, solid phase, and nonsettleable particulate or macromolecular phase. This latter phase is likely to be mobile in some porous media, due to the small particle sizes involved. Voice et al. [1983] have also raised serious doubts



about the field applicability of batch adsorption measurements of the distribution between a dissolved and a solid phase. In particular, their study of the adsorption of chlorinated hydrocarbons onto lake sediments indicated the presence of colloidal or microparticulate (i.e., nonsettleable) material that adsorbed the chlorinated hydrocarbon but could not be separated from dissolved compounds.

The fact that strongly sorbing hydrophobic compounds and macromolecules are mobile in soil systems has been demonstrated in the laboratory and observed in the field. Soil column experiments conducted by *Vinten et al.* [1983] have shown that fine particles can transport pesticides into soil. Paraquat adsorbed to clay and DDT adsorbed to sewage solids migrated into their soil columns; actual migration depended on particle and aqueous chemistry that controlled particle aggregation and deposition. In the field, DDT and the pesticide napropamide have been observed to migrate to depths much greater than expected. *Enfield et al.* [1982] compared equilibrium partitioning model simulations with field data for DDT 10 years after application and found discrepancies which cast grave doubt on the suitability of this type of model for such highly sorbing compounds such as DDT. Both laboratory and field data collected by *Jury et al.* [1986] lead the authors to similar conclusions, as a small amount of the napropamide appears to travel through soil at a rate inconsistent with the adsorption equilibrium assumption. In fact, small quantities of napropamide traveled at the average velocity of the pore water in the laboratory columns. *Robertson et al.* [1984], in a field study of aquifer contamination by waste pulp liquor, found that the macromolecules tannin and lignin moved up to 900 m horizontally from the discharge site over an 11-year period. The migration rate approached the average linear groundwater velocity of the area. In a study by *Page* [1981] of New Jersey surface and groundwater quality, groundwaters were at least as contaminated as surface waters with toxic chemicals, providing evidence of the mobility of hydrophobic and other compounds despite their sorption tendencies.

**2.1.3. Radionuclides and metals.** The approach generally taken to predicting radionuclide and other metal transport in porous media is similar to that adopted for organics transport discussed above. Radionuclide batch adsorption experiments with soil have been used to determine distribution coefficients for prediction of retardation in continuous flow columns and aquifers. However, *Reynolds et al.* [1982] found that batch adsorption studies for cesium and strontium underestimated migration observed in columns, while *Coles and Ramspott* [1982] found much more rapid migration of ruthenium in the field than expected from batch adsorption results. For some time, researchers have recognized that particles and colloidal material could transport radionuclides much greater distances than expected from adsorption predictions. *Champlin and Eichholz* [1968] have suggested that fine particle transport may be a significant mode of radionuclide migration. They measured clay particle migration through a fine sand with a fluid flow velocity of 1.2 m/d. Radiolabeled clay and bacteria were found to penetrate only 20 cm after 7 days of flow, but flow of a detergent solution through the sand bed was able to remobilize the adsorbed tracers at a velocity comparable to the fluid flow velocity [*Champlin and Eichholz*, 1976]. Work by *Shepard et al.* [1980] demonstrated that submicrometer colloidal material in soil was important in binding radionuclides, as

was also observed in chlorinated organic partitioning discussed above. Laboratory experiments of *Higgo and Rees* [1986] suggest a particulate-associated phase in batch actinide sorption experiments. *Nelson et al.* [1985] found that colloidal organic carbon (COC) competed with lake sediment for binding plutonium, such that measured distribution coefficients decreased with increasing COC concentration.

Nonradioactive metals are similarly associated with colloidal material. Analytical methods designed to distinguish "dissolved" from "particulate-associated" metals in natural waters have frequently resorted to filtration through a filter capable of retaining particles greater than 0.1 to 1  $\mu\text{m}$ . *Sheldon and Sutcliff* [1969] established that pore sizes of membrane, glass fiber, and silver filters decreased as filter retention of particulate matter much smaller than pore size increased. *Johnson and Wangersky* [1985] verified these results and proposed means of distinguishing between dissolved and particulate matter that minimize the retention of particles smaller than pore size. *Danielsson* [1982] conclusively showed that various commercial filters removed "dissolved" iron and organic matter after some volume had passed through the filters. Iron concentrations in the filtrate decreased by over an order of magnitude as the filters were clogged by colloidal matter containing iron.

**2.1.4. Asbestos fibers.** While there is no direct evidence to link asbestos fibers in drinking water with disease, there is concern over asbestos fiber levels in water supplies originating in serpentine rock. Recent field monitoring of a groundwater aquifer in California recharged from a reservoir situated in serpentine rock found asbestos fiber levels from 20 to 1 million fibers per liter [*Hayward*, 1984]. The reservoir water contained 3100 million fibers per liter, indicating some attenuation or dilution of fibers. The fiber level of these groundwater samples was classified as high compared to fiber concentrations ranging from 0.4 to 25 million fibers per liter estimated to cause one extra case of cancer in 100,000 persons over a 70-year life span.

## 2.2. Surface and Subsurface Wastewater Treatment, Disposal, and Recycling

Land has long been in use as a means to treat and dispose of sewage. The artificial recharge of groundwater has provided a means of recycling treated sewage effluents and increasing groundwater storage. The operation of these systems depends heavily on the ability of water to infiltrate the soil or aquifer material over long time periods without reducing permeability, but to attenuate pollutant migration.

**2.2.1. Surface and subsurface treatment of sewage.** The goal in the design of land treatment systems for sewage is to achieve degradation of organic wastes and for wastewater disposal in permeable soils while avoiding surface ponding. Laboratory research has been directed toward investigating factors which control clogging or permeability reduction in soil columns. *Daniel and Bouma* [1974] conducted a laboratory study using undisturbed soil cores to examine the effect of carbon loading, in terms of chemical oxygen demand (COD) and biochemical oxygen demand (BOD), on soil clog. Septic tank effluent was compared with tank effluent following extended aeration biological treatment. The extended aeration treatment converted soluble organic carbon into bacterial cells that more rapidly clogged the soil column than the original effluent. A study by *Kristiansen* [1981] dealt with relation-



ships between clogging and physical and chemical characteristics of the soil environment, again in a qualitative manner. Dissolved oxygen content and biodecomposition potential of the soil environment were reduced following application of septic tank effluent. Surface ponding occurred following clogging and further reduced dissolved oxygen penetration into the soil. Based on a field study of wastewater injection, Oberdorfer and Peterson [1985] propose that production of nitrogen gas by microbial denitrification dominated clogging. These studies suggest that chemical and biological processes as well as physical clogging phenomena control the suitability of soil for wastewater treatment and disposal. The U.S. Environmental Protection Agency [1977] Process Design Manual has an extensive review of the physical, chemical, and biological processes important during land treatment. Design of such systems is heavily dependent on field tests.

**2.2.2. Artificial recharge of groundwater.** Water resource management and wastewater reclamation are increasingly relying on artificial recharge of aquifers [Asano, 1985]. Recharge can be accomplished via surface spreading basins if there is a surface stratum, or via injection wells if the aquifer is below an impermeable layer. Recharge operations can be hampered if hydraulic permeability is reduced by particle capture, microorganism growth, or chemical precipitation reactions. Laboratory experiments and field data are available, but rarely can the mechanisms promoting permeability reduction be quantified or isolated. In field experiments conducted by Sniogocki [1963], permeability reduction, following well injection of treated wastewaters, was related to air entrainment, presence of suspended particles, microorganism growth, and chemical precipitation reactions.

The importance of straining and cake filtration mechanisms has been recognized for some time in recharging turbid water through soils [Behnke, 1969; Rahman et al., 1969]. Goss et al. [1973] provided field data demonstrating the importance of soil macropores in significantly increasing the depth of particle penetration. In a recharge basin tilled to destroy naturally occurring macropore openings, 50% of the particle mass present in the recharge water was retained in the top centimeter of the soil during a 44-day test. Basin permeability is typically restored following drying and removal of 0.15 cm of surface material. In a recharge basin containing naturally occurring macropores of size 0.01 to 0.1 cm, 50% of the particle mass was retained in the top 46 cm during 26 days of recharge. Kovenya et al. [1972] studied the importance of particle size relative to soil media size in controlling particle migration under saturated and unsaturated flow conditions. They found that 1- and 10- $\mu\text{m}$  particles were removed by cake and straining mechanisms at the surface while the smallest particles of diameter 0.1  $\mu\text{m}$  were removed by adsorption. They noted greatest migration for 0.5- $\mu\text{m}$  particles.

Permeability reduction in soil systems and porous formations as a result of ionic strength alterations is an important consideration in groundwater recharge as well as in oil and gas recovery. Such reduction occurs when electrolyte concentrations are sufficiently low to cause swelling and/or deflocculation of clay particles within soil or formations [Hardcastle and Mitchell, 1974; Goldenberg et al., 1983]. The results of both swelling and dispersion caused by changes in aqueous chemistry have been observed in field and laboratory studies. Nightingale and Bianchi [1977] describe the leaching of sub-micrometer particles from surface soils when relatively low

averaged 10 mg/L in the groundwater after recharge, substantially more than the 3 mg/L present in the low salinity recharge water. The explanation for the observed increase in turbidity was that flocculated particles present in the sandy loam soil were dispersed following introduction of low ionic strength water that dispersed the particles, breaking up the flocs in the soil. Whether or not clay swelling took place was not addressed in this study.

Although soil permeability was not perceivably altered by particle movement in the Nightingale and Bianchi [1977] study, porous media permeabilities have been found to depend on the ionic composition of the flowing fluid. Goldenberg et al. [1983, 1984] found that the permeability of a sandy aquifer containing clay particles decreased by orders of magnitude when seawater was replaced by a local groundwater with a conductivity of 780  $\mu\text{mho/cm}$ , or approximately 350 mg/L of total dissolved salts. Since no clay particles were observed in column effluents, the results were interpreted as an alteration of clay particle aggregates within the porous media into less permeable structures at the lower salt concentrations. The low permeabilities caused by the low salt groundwater could not be restored by flushing with seawater and were apparently related to the presence of montmorillonite [Goldenberg et al., 1984]. Thus the low salt recharge water used by Nightingale and Bianchi [1977] was able to disperse and mobilize clay particles, while the higher salt content of the aquifer recharge water used in Goldenberg et al.'s experiments apparently did not result in particle mobilization but did result in permeability reduction due to swelling.

Hardcastle and Mitchell [1974] reported on laboratory experiments simulating conditions in sediments of a coastal groundwater basin which also demonstrated that permeability changes occur with changes in electrolyte concentration in pore water. Although some permeability reduction as a result of decreased electrolyte concentration could definitely be attributed to swelling of clays, the authors attributed erratic variations in hydraulic conductivity at electrolyte concentrations below 0.05 N (3000 mg/L) to migration of dispersed clay particles and subsequent pore plugging.

Morris and Sheppard [1982] experimented with sandstone cores containing both swelling (illite-smectite) and nonswelling (kaolinite) clays. They measured permeability reduction as a result of injection of a nonpolar solvent (kerosene) and polar solvent (water). They found that a largely irreversible permeability reduction occurred following injection with kerosene which they attribute to pore plugging by mobile clay particles. These mobile particles were believed to be kaolinite, which generally occurs as discrete particles in pore spaces, unlike illite, which occurs as a relatively continuous mineral coating of pore walls to which it is firmly attached. Permeability reduction which occurred after injection with the polar liquid was attributed to the swelling clays, as it was largely reversible. Thus the type of clay present and the pore fluid composition are important in determining whether significant permeability reduction will occur in soil systems and porous formations.

Khilar and Fogler [1984] demonstrated the existence of a critical salt concentration (CSC) for particle dispersal in a Berea sandstone core. The CSC, defined as the concentration below which particles will be released from the sandstone, only existed for monovalent cations and was found to depend on temperature and type of cation. For sodium chloride, a CSC of 0.071 M (4160 mg/L) was found.

Besides suspended particles, recharge of dissolved sub-



stances can result in permeability reduction if the substance promotes particle formation. *Okubo and Matsumoto* [1983] have found that recharging wastewater effluents for long time periods requires suspended solids less than 2 mg/L and total organic carbon less than 10 mg/L to prevent growth of micro-organism films. *Wood and Bassett* [1975], in a field study of a surface spreading operation, found that the growth of anaerobic organisms could cause a significant decrease in hydraulic conductivity as well as change the pH, bicarbonate, and sulfate concentrations. *Warner* [1966] conducted laboratory experiments on chemical precipitation reactions that could occur when injected waste solutions mix with existing groundwater. Formation of  $\text{BaSO}_4$  and  $\text{CaSO}_4$  crystals had no effect on permeability while more porous precipitates of amorphous  $\text{Fe}(\text{OH})_3$  resulted in a 30% reduction in permeability under their conditions.

### 2.3. Petroleum Extraction

In the removal of petroleum from underground reservoirs, both encouragement and avoidance of porous media clogging are of interest. One of the functions of drilling muds is to seal up the shaft as it is drilled, preventing loss of drilling mud. Sealing is achieved by addition of clays and chemicals that prevent clays from aggregating. As fluid flows into porous formations, clays individually deposit, and a low permeability filter cake is formed. There are a number of other constraints in the preparation of drilling muds that result in a very empirically based design [see *van Olphen*, 1977].

Extraction of petroleum from a formation can be hindered by the presence of formation fines, small particles present in pore spaces of the reservoir rocks. *Muecke* [1979] conducted experiments that characterized these particles and measured the movement of fines in single- and multiple-phase flow in a sandstone reservoir. Fines were classified as particles less than 37  $\mu\text{m}$  and, in unconsolidated sandstones, represented at least 2–15% by weight of the formation. These particles were observed to coat the sand grains and were found to contain only 11% clay by weight. From the single-phase flow experiments, straining at pore spaces appeared to be the only immobilizing mechanism for fines. The particles retained at flow restrictions could be remobilized by changes in flow rate and direction. In experiments with two immiscible liquids, it was found that particles only move when the phase that wets them is mobile.

In sandstone formations, water sensitivity, or permeability reduction following displacement of natural waters with less saline water, has been recognized for some time. The problem is of concern to the petroleum industry mainly from the standpoint of water flooding operations. *Khilar and Fogler* [1983] observed 2 orders of magnitude decrease in permeability following flow of two to three pore volumes of freshwater through a sandstone core. They developed a conceptual model based on dispersal of clay aggregates within the sandstone by the fresh water. The dispersed clays were rapidly strained out in pore restrictions, causing a rapid decrease in permeability. Changes in freshwater flow direction temporarily increased the permeability, but reduced permeability was quickly reestablished as pores strained out the mobilized clay particles. Introduction of salt water, with flow reversal, quickly restored most of the original permeability as the clay aggregated and was filtered out by physical-chemical processes. This model agrees with *Harcastle and Mitchell* [1974] but differs from *Goldenberg et al.*'s [1983] interpretation of aquifer permeability reduction by fresh water. Insufficient characterization of *Khilar*

and *Fogler*'s [1983] sandstone, clays, and fresh water prevents resolution of the discrepancy in descriptions.

Closely related to particulate behavior in sandstone formations is the flow of emulsions in porous media. *McAuliffe* [1973] has discussed the use of oil droplets to block high permeability regions and force water into less permeable regions. Permeability reduction depended on emulsion droplet size with larger droplets being much more effective in permeability reduction than smaller ones. Continuous flow experiments achieved a 12- to 35-fold permeability reduction when at most 6% of the pore volume was occupied by oil droplets under constant flow conditions.

More recently, emulsion flow through porous media has been modeled as a filtration phenomenon rather than non-Newtonian emulsion flow. *Schmidt et al.* [1984] and *Soo and Radke* [1984a, b] observed that permeability reduction was caused by stable emulsion capture by the media and the retained droplets could only be released by an increase in flow velocity. Droplet size controlled equilibrium permeability reduction, and a model based on droplet filtration within the porous media could be fitted to the data [*Soo and Radke*, 1986; *Soo et al.*, 1986].

### 2.4. Hydrogeologic Systems

Colloid and particle transport occurs in many natural and altered hydrogeologic systems. These systems are characterized by chemical disequilibrium caused by changes in temperature, pressure, and oxidation/reduction potential. The resulting chemical reactions caused either precipitation of mineral phase or transformation of one mineral phase to another. The transport of these minerals is of concern either as colloidal intermediates or as distinct solids suspended in fluid.

The diagenesis of silica from an amorphous phase to crystalline quartz follows a dissolution-reprecipitation pathway which is affected by pore water diffusion rates among other factors [*Williams and Crerar*, 1985]. The pathway involves formation of polymers, the flocculation of which yields intermediates in the transformation process. The fate of both polymers (~1 to 5 nm diameter) and flocs (up to 1  $\mu\text{m}$  diameter) is governed by colloidal, hydrodynamic, and physical-chemical forces.

In the formation of soil profiles, colloid and particle transport are two of many processes inferred to occur based on analysis of laboratory and field data. *Birkeland* [1984] has reviewed these processes and notes the difficulty of isolating specific processes that control the translocation of iron, aluminum, clay minerals, and organic matter. The variety of naturally occurring soil types makes generalizations difficult, but the concepts of colloidal stability figure prominently in explanations of observed soil profiles. That is, aqueous pH and ionic composition control clay and organic matter aggregation and attachment. Straining of clay particles by soil pores is also mentioned. *Pilgrim and Huff* [1983] found that rainfall impact on soil aggregates released particles into suspension, and the transport of the 4- to 8- $\mu\text{m}$  particles was through soil macropores. They recorded suspended sediment concentrations of over 1000 mg/L in subsurface flows. Clay particle migration, again in macropores, has also been implicated in the transport of organic carbon deep into the unsaturated zone above the Ogallala aquifer [*Wood and Petraitis*, 1984]. It is hypothesized that such particulate flux is a part of the carbon cycle involving gaseous, liquid, and solid transport processes.



In the area of hydrothermal ore body formation, considerable uncertainty exists as to the sources, transport, and deposition of metallic sulfides (see, for example, *Ohle* [1980] and *Skinner* [1979]). *Horzempa and Helz* [1979] have found that colloidal copper sulfide prepared by precipitation is destabilized by the ionic composition of natural waters. Transport of the colloids could then be dominated by aggregation and attachment in porous media.

Natural and engineered systems involving fluid transport of heat through porous media can result in mineral dissolution followed by precipitation and media permeability reductions. In laboratory studies of fluid flow through granite cores held in a temperature gradient, permeability decreased to 1.5% of the original permeability as minerals dissolved at higher temperatures and then precipitated within the lower temperature region of the core [*Moore et al.*, 1983]. In geothermal energy recovery, cooled brines are reinjected into the formation only after reducing the potential for scale formation. Scale from the precipitation of silica, calcium carbonate, and various sulfates can deposit in the piping system, near the injection well, or in the formation. *Weres and Apps* [1982] have reviewed the literature on chemical transformations during brine reinjection and note that predictions of mineral phase equilibrium and scale formation potential are possible. Laboratory and field experiments are required to determine permeability alterations and to evaluate methods of restoring permeability after well or formation damage. Minerals can precipitate on pipe surfaces, on the formation particles, and also on suspended particles present in geothermal fluids. Conventional treatment processes for particle removal and inhibition of scale formation are also reviewed by *Weres and Apps*, although treatment criteria for brine reinjection are not firmly established. In calculations of mineral phase equilibrium within aquifers used for thermal energy storage, *Palmer and Cherry* [1984] report that  $\text{CaCO}_3$  (calcite) will precipitate following an increase in temperature of groundwater, resulting in either scaling of the piping system or accumulation within the aquifer after reinjection. By assuming a distance over which the precipitated calcite will deposit, permeability reductions were roughly estimated at 2 orders of magnitude.

### 2.5. Sealants and Barriers

Introduction of small particles into porous media for the specific purpose of permeability reduction has been considered in sealing unlined canals and reservoirs besides oil well shafts mentioned previously. *Curry and Beasley* [1962] conducted experiments to test such reduction using clay particles flowing through uniformly sized media under aqueous chemical conditions that did not aggregate the clay particles. Porous media permeability reduction was caused by mechanical straining of the clay particles by the media. Fine media (0.063, 0.080, and 0.163 mm diameter) were much more efficient at capturing the clay than coarser media (0.385 and 0.775 mm), with more sealing observed at higher imposed hydraulic gradients. *Rausch and Curry* [1963] also used clay suspensions in porous media to test sealing potential as a function of salinity and hydraulic gradient. The investigators found that the degree of sealing attained, as measured by reduction in discharge, increased with sodium saturation of the bentonite mineral and with hydraulic gradients up to 1.0 cm/cm.

Clays have also been used to isolate waste disposal sites from the hydrologic cycle via low permeability liners and caps. One option under consideration for isolation of radionuclides

is to surround a waste canister with packed clay in a geologically stable formation. The clay is intended to provide an adsorptive barrier as well as reduce permeability of the site to groundwater. *Le Bell and Stenius* [1980] have shown that natural groundwater coagulated a bentonite clay, a proposed buffer for nuclear waste canisters deposited in bedrock. Migration of radioactive material adsorbed to the buffer through rock fissures would then be inhibited by attachment of the coagulated clay particles onto fissure surfaces. Laboratory experiments by *Vandegrift et al.* [1984] found significant bentonite retention in basalt fissures. *Shade et al.* [1984] discussed preliminary experiments on the adsorption of radionuclides to silica rich colloids released from glass waste containers. These colloids were not destabilized by the natural groundwater considered, although the authors did not attempt a complete characterization of colloids. *Avogadro and de Marsily* [1983] and *Saltelli et al.* [1984] determined that americium-containing colloids were leached from a simulated waste container. Colloids were determined to be in the size range of 0.05–1  $\mu\text{m}$  by membrane filtration. The colloidal americium was retained within a porous media column along with adsorbed americium.

Sand and gravel filters are used as barriers to particle migration in dams and in excavation dewatering. In both cases, filters are designed to prevent the loss of particulate core material by erosion, or piping, as well as provide adequate drainage to prevent buildup of pore pressure. Graded filters are sometimes used, with finer layers to prevent piping and coarser layers with significant permeability to allow good drainage. The design gradation of the filters is generally based on criteria derived empirically from laboratory tests [*Cedergren*, 1977; *Sherard et al.*, 1984a, b] and summarized in the next section on straining.

## 3. FILTRATION MECHANISMS AND WATER FILTRATION EXPERIENCE

The previous literature review has demonstrated that particles and associated pollutants can be transported by fluids in porous media. The purpose of this section is to discuss the three filtration mechanisms in Figure 1 and review the applicability of mechanistic filtration theories to groundwater systems. A mechanistic analysis of particle transport through porous media is predominately based on developments in the separation science literature within chemical engineering, mineral processing, and water treatment. In these engineering fields the control of particle collection mechanisms is possible through selection of process variables such as media size, flow rate, chemical treatment, and particle size. Even so, design of particle collection systems is heavily dependent on parameters that cannot be predicted theoretically. Thus a completely predictive model of particle transport through porous media should not be expected.

By no means is this review intended to be exhaustive, since the filtration literature with its proposed theories and empirical data is extensive. References are given to applicable review articles, and generalizations of theoretical and experimental results are given here to allow a preliminary evaluation of conditions favoring and hindering particle transport in the hydrogeologic environment.

### 3.1. Surface Filtration

The collection of particles and aggregates above porous media or fibrous mats is termed either cake, surface, or



vacuum filtration and occurs when particles are too large to penetrate into the media. The process is commonly used to dewater concentrated slurries and is usually avoided in deep bed, granular media filtration. The analysis of surface filtration is based on the accumulation of a permeable filter cake above the media as particles are retained. Under constant pressure the flow through this filter cake decreases with time as the cake thickens and the porosity decreases during compression. Cheremisinoff and Azbel [1983] provide a review of surface filtration practice, and Willis and Tosun [1980] discuss current surface filtration theory. Filter cakes can have a very low permeability; Willis and Tosun report that a 2-cm-thick filter cake composed of fine clay had a head loss of 30 m of water, or a hydraulic gradient of 1500. Filter cake permeability is known to be a function of particle aggregation with destabilized flocs having the most open, porous structure and thus a higher permeability compared to cakes formed from stable suspensions [Smellie and LaMer, 1958]. Since hydrostatic pressures under natural flow conditions are limited, filter cakes can be viewed as becoming rapidly impermeable. During groundwater recharge the practice of surface drying followed by disruption or removal is one approach used to restore sites of recharge that can become clogged by a surface cake.

### 3.2. Straining Filtration

While a straining mechanism is frequently mentioned as the cause of suspended particle removal within groundwater, little quantitative analysis has been attempted. Sakthivadivel [1969] carefully acquired laboratory data on particle capture by porous media and the resulting reduction in permeability. Sakthivadivel's experiments were conducted with large plastic particles suspended in mineral oil to minimize any particle-particle and particle-media interactions. The most critical factor determining straining within porous media was the ratio of the media diameter to the particle diameter,  $d_m/d_p$ . For  $d_m/d_p$  less than 10, or relatively large particles compared to the media size, no particle penetration into the media was observed, that is, cake filtration. Within the narrow window of particle size  $10 < d_m/d_p < 20$ , he found permeability reductions by a factor of 7–15, and deposited particles occupied greater than 30% of the pore volume. Particle deposit was probably much greater near the surface, but Sakthivadivel's data on deposit volume are averaged over the 45-cm column depth. For relatively small particles,  $d_m/d_p > 20$ , only 2–5% of the pore volumes were occupied by retained particles under equilibrium conditions, and permeability reductions were limited to only 10–50% of the clean porous media value. If influent particle size distributions contained a broad distribution in sizes from  $d_m/d_p < 10$  to  $d_m/d_p > 20$ , then retained larger particles acted as strainers for smaller particles, leading to effective particle filtration at or near the media surface in a combination of surface and straining filtration. Herzig et al. [1970] considered particle capture by straining as a purely geometrical process and claimed that little straining was expected for  $d_m/d_p > 12$ . Their analysis predicts that 0.53% of the bed volume could be occupied by particles in crevices if  $d_m/d_p = 20$ , but only 0.053% for  $d_m/d_p = 50$ . In preliminary experiments, Sakthivadivel [1966] found that deposited particles could not be dislodged if the flow rate was increased. Flow reversal did resuspend deposited particles.

Sakthivadivel's results on straining have been confirmed by tests of geotechnical filter materials constructed of sands

where the size distributions of the larger media and the smaller media were taken into account. Sherard et al. [1984a] found that finer sand would not penetrate coarser sand during water flow or vibration if

$$d_{m,15}/d_{p,85} < 9 \quad (1)$$

where 15% by weight of the coarse filter media had a diameter less than or equal to  $d_{m,15}$  and 85% by weight of the finer sand particles had diameters less than or equal to  $d_{p,85}$ . Equation (1) was based on experiments conducted over a range in  $d_{m,15}$  from 1 to 10 mm. Filter criteria based on average coarse and fine media sizes were not acceptable, and the above criterion was successful for a range of coarse and fine sand size distributions. For the straining of silts and clays by sand filters, similar criteria were developed that also depended on soil cohesiveness [Sherard et al., 1984b].

### 3.3. Physical-Chemical Filtration

Particles much smaller than the media size are retained only if attractive forces dominate when particles collide with media. Since particulate pollutants (bacteria, viruses, asbestos fibers) and colloidal matter having a high sorption capacity for pollutants are micrometers and smaller in size, the ratio of media size to particle size,  $d_m/d_p$ , for sand and gravel aquifers exceeds 1000. Particle retention, if any, will be dominated by physical-chemical filtration. The discussion of physical-chemical filtration includes aspects of (1) particle-media collision mechanisms, (2) particle-media attachment mechanisms, (3) removal kinetics for clean media, and (4) removal kinetics during clogging where particle attachment to previously collected particles dominates.

3.3.1. Collision mechanisms. Figure 2, from Yao et al. [1971], illustrates the three dominant transport mechanisms of suspended particles flowing through porous media. The fluid in Figure 2 is flowing at an approach velocity  $U$  in the same direction as gravity. For very small particles, less than a few micrometers, the dominant transport to the media surface is via Brownian motion of the particles and is characterized by a particle diffusivity  $D_p$  originally derived by Einstein,

$$D_p = kT/3\pi\mu d_p \quad (2)$$

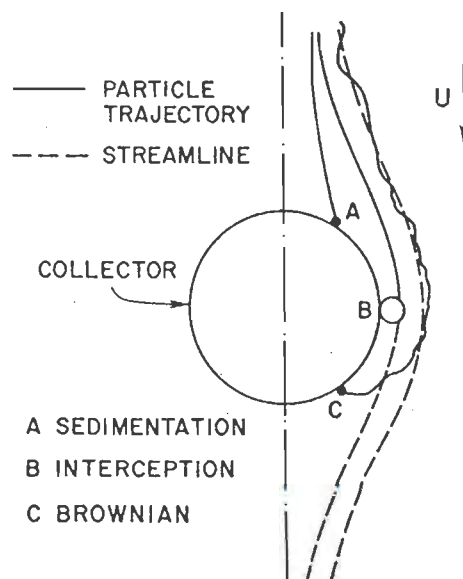


Fig. 2. Three dominant transport mechanisms of suspended particle transport to a collector surface [from Yao et al., 1971].



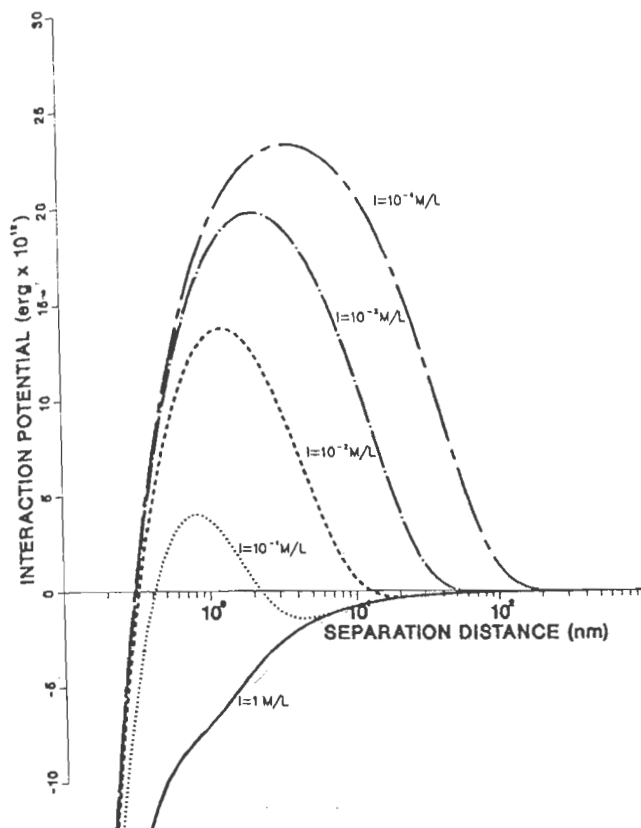


Fig. 3. The net interaction potential for a 1.0- $\mu\text{m}$  sphere approaching a flat plate at different ionic strengths. The surface potentials for the plate and particles were  $-30\text{ mV}$ .

where  $k$  is the Boltzmann constant,  $T$  absolute temperature, and  $\mu$  fluid dynamic viscosity. For water at  $20^\circ\text{C}$  the Brownian diffusivity for a  $1\text{-}\mu\text{m}$ -diameter particle is  $4.3 \times 10^{-9}\text{ cm}^2/\text{s}$ , which is small but significant within pore spaces.

Particles following fluid streamlines may collide with the media by means of interception, a function of an interception parameter

$$(d_p/d_m)^2 \quad (3)$$

for spherical particles and media. For a particle with a density different than the suspending fluid, gravitational sedimentation can cause particles to deviate from fluid streamlines and collide with the media surface. The parameter controlling gravitational sedimentation is the Stokes settling velocity of the spherical particle,

$$v_s = \frac{g}{18\mu} (\rho_p - \rho_f) d_p^2 \quad (4)$$

where  $g$  is the gravitational acceleration and  $\rho_p$  and  $\rho_f$  are the particle and fluid densities, respectively. For particles suspended in gases, inertial impaction is an important mechanism, but not so for particles in water [Spielman, 1977].

**3.3.2. Attachment mechanisms.** Particles colliding with a fixed media surface do not always attach because of electrostatic, chemical, and hydrodynamic forces that operate at very small separations between particles and media. The dominant force controlling attachment is the electrostatic interaction between a charged particle and a charged media surface. Particles and media in natural waters possess surface potentials  $\psi_p$  and  $\psi_m$ , resulting from isomorphic substitution within the crystal lattice, surface group ionization, and ion

adsorption. The magnitudes of the surface potentials are often characterized by the zeta potential of the particle,  $\zeta_p$ , or the media,  $\zeta_m$ , representing the electrostatic potential at the plane of shear [Hunter, 1981]. While particle surface chemistry controls surface charge and zeta potential, predictions of particle-media interaction based on surface chemistry models are in the developmental stage [James and Parks, 1982; O'Melia, 1985, 1986].

Because counterions in solution accumulate in a diffuse double layer surrounding suspended particles and fixed media, the electrostatic charge becomes masked at a sufficient distance away from the particle or media surface. The characteristic thickness of the diffuse layer of charge is denoted by  $\kappa^{-1}$  and is given by

$$\kappa^{-1} = \left[ \frac{ekT}{8\pi e^2} \left( \frac{10^3}{NI} \right) \right]^{1/2} \quad (5)$$

where  $\epsilon$  is the dielectric constant of the fluid,  $e$  the charge of an electron,  $N$  Avogadro's number, and  $I$  ionic strength for a monovalent salt. For water at  $20^\circ\text{C}$ , (5) simplifies to

$$\kappa^{-1} = 3.0 \times 10^{-8} I^{-1/2} \text{ cm} \quad (6)$$

where the units of ionic strength are moles per liter. As the ionic strength increases, the diffuse layer thickness is compressed, and electrostatic forces between a colliding particle and the media surface are only operative at short separations. For particle interactions with a fixed media grain, where  $d_m/d_p \gg 1$ , the interaction potential of the double layers may be approximated by

$$\phi_{dl} = \frac{\epsilon d_p}{2} \psi_p \psi_m \ln(1 + e^{-\kappa h}) \quad (7)$$

after Spielman and Cukor [1973], where repulsive potentials are assumed positive and  $h$  is the separation distance between the surface of the particle and the surface of the media. Equation (7) is valid for  $|\psi_p| \approx |\psi_m| < 50\text{ mV}$  and for  $\kappa d_p > 10$ , reasonable for situations encountered in natural waters.

Besides electrostatic interactions between particles and media, there are also attractive forces from dipole-dipole attractions between atoms and molecules called London-van der Waals forces. The attractive interaction potential between a sphere and a flat plate is given by [Spielman and Cukor, 1973]

$$\phi_a = \frac{A}{6} \left[ \ln \left( \frac{h + d_p}{h} \right) - \frac{d_p}{h} \frac{h + d_p/2}{h + d_p} \right] \quad (8)$$

where  $A$  is Hamaker's constant with typical values in the range of  $10^{-13}$  to  $10^{-12}\text{ erg}$  [Overbeek, 1952; Ives and Gregory, 1966]. Theoretical calculations of the Hamaker constant are possible, but usually the value is obtained by fitting experimental data to theoretical expressions from which the Hamaker constant is obtained [Ives and Gregory, 1966]. Additional particle-media and particle-particle attractive and repulsive forces result from specific chemical interactions between surface groups. Such factors are dominant in water filtration technology employing chemical coagulants [O'Melia and Stumm, 1967] and in natural waters where adsorbed organic matter coats mineral surfaces [Hunter and Liss, 1982]. Quantification of these chemical interactions has proved difficult in general and is not considered further in this review.

The addition of the repulsive and attractive forces during particle collisions with media surfaces leads to an interaction potential that is highly dependent on ionic strength. Figure 3



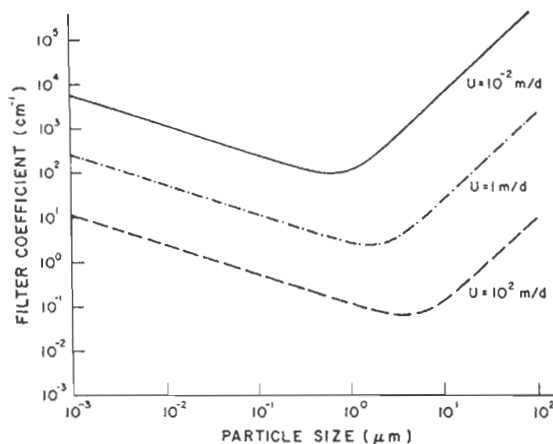


Fig. 4. Predicted clean bed filter coefficients from equation (11) for three groundwater flow velocities, assuming  $A = 10^{-13}$  erg,  $d_m = 0.1$  cm, and  $\rho_p = 1.5$  g/cm<sup>3</sup>.

illustrates the net interaction potential of a 1- $\mu$ m spherical particle with  $\psi_p = -30$  mV, colliding with a flat plate having a surface potential of  $\psi_m = -30$  mV for ionic strengths from  $10^{-4}$  to  $1.0$  M. At an ionic strength of  $10^{-4}$  M the thick diffuse layer causes electrostatic repulsion to dominate at separations between 0.3 nm (3 Å) and about 200 nm. At intermediate ionic strengths, the diffuse layer is compressed, and the "secondary minimum" is more pronounced where the London-van der Waals attractive force dominates over electrostatic repulsion. An energy barrier exists that can prevent particles from approaching the media surface in the "primary minimum" ( $h \rightarrow 0$ ). At an approximate ionic strength of  $0.5$  M, the diffuse layer thickness is compressed such that the London-van der Waals force dominates at all separations and there is no energy barrier to particle-media attachment. As indicated in Figure 3, the separation distances between particle and media surfaces are much smaller than the particle size, supporting the usual distinction between particle transport mechanisms and particle-media attachment. The depth of the primary minimum is not infinite because of Born repulsion between electronic clouds at very close approaches.

Actual particle-media attachment is coupled with particle transport mechanisms when an energy barrier or a secondary minimum exists. Classical colloid stability theory has considered the approach of particles to an energy barrier with the Brownian motion of the particles causing a distribution of thermal energies [Overbeek, 1952] leading to the particle attachment rate being less than the particle transport rate. In general, the secondary minimum must be sufficiently deep (several  $kT \approx 10^{-13}$  erg) to influence attachment, and such attachment is considered reversible [Overbeek, 1952]. For larger particles with transport dominated by interception, Spielman and Cukor [1973] have calculated particle trajectories leading to particle attachment in primary and secondary minimums. Their theoretical analysis predicts that under very low fluid velocities, particles may be retained in the secondary minimum as indicated in Figure 4. The transition from nonattachment to complete attachment can be accomplished over very small changes in particle surface properties or changes in aqueous chemistry based on theoretical calculations for Brownian collection [Ruckenstein and Prieve, 1973; Spielman and Friedlander, 1974] and interception-dominated collisions [Spielman and Cukor, 1973].

Besides electrostatic and London-van der Waals forces, the

hydrodynamic force of squeezing out water to permit particle-media attachment is also important. Spielman [1977] has reviewed the importance of hydrodynamic factors which may cause a factor of 10 decrease in attachment compared to an analysis ignoring the effect.

**3.3.3. Clean media removal kinetics.** The purpose of studying particle removal kinetics during filtration is to ultimately predict particle migration through porous media and resulting alteration of media by the retained particles. The kinetics of particle retention are first considered for clean media without any deposited particles altering the media surface or fluid flow. Under specific circumstances, clean media theory and experimental data are in good agreement. The following section then considers particle accumulation within porous media where the deposited particles substantially alter porous media permeability.

The basic filtration equation empirically proposed by Iwasaki [1937] recognized that particle removal from solution was first order in particle concentration

$$dC/dx = -\lambda_0 C \quad (9)$$

where  $C$  is particle mass concentration in the fluid phase,  $\lambda_0$  is the clean bed filter coefficient, and  $x$  is the distance along the direction of flow. The filter coefficient was typically evaluated by measuring the particle concentration after flow through a filter of length  $L$  and backcalculating  $\lambda_0$  from the integrated form of (9),

$$C(L) = C_0 e^{-\lambda_0 L} \quad (10)$$

where  $C_0$  is the influent particle concentration. Initial attempts at relating  $\lambda_0$  to particle, media, and flow properties were widely divergent since usually only suspension concentration was measured and influent particle size distributions were poorly known [see Ives, 1970]. Equation (9) only applies for a suspension uniform in size, or monodisperse, since particle capture is strongly dependent on particle size as discussed below.

A mechanistic understanding of clean bed filtration has followed advances in the aerosol filtration literature through research by Yao et al. [1971], Spielman and FitzPatrick [1973], and others, as summarized by Tien and Payatakes [1979]. Particle trajectories have been calculated during flow through porous media with particle capture by Brownian motion, interception, and gravitational sedimentation. The results of the numerical simulations gave clean bed filter coefficients that were described by the empirical equation

$$\lambda_0 = \frac{3}{2} \frac{(1-p_0)}{d_m} \left[ 4A_s^{1/3} \left( \frac{U d_m}{D_p} \right)^{-2/3} + 0.56 A_s \left( \frac{A}{\mu d_p^2 U} \right)^{1/8} \left( \frac{d_p}{d_m} \right)^{15/8} + 2.4 \times 10^{-3} A_s \left( \frac{v_s}{U} \right)^{1.2} \left( \frac{d_p}{d_m} \right)^{-0.4} \right] \quad (11)$$

where  $p_0$  is the media porosity and  $A_s$  is a parameter correcting particle capture by a single isolated collector for capture within a packed porous media with

$$A_s = \frac{1 - P^5}{1 - \frac{3}{2}P + \frac{3}{2}P^5 - P^6} \quad (12)$$

where  $P = (1 - p_0)^{1/3}$ .



Equation (11) assumes that the particle capture mechanisms of Brownian motion, interception, and gravitational sedimentation are additive. The first term on the right-hand side of (11) accounts for particle collection by Brownian diffusion, with the filter coefficient proportional to  $d_p^{-2/3}$  when particle diffusivity from (2) is substituted. The second term within the brackets of (11) accounts for interception collection and contains a weak dependence on the Hamaker constant and the flow velocity. Gravitational sedimentation is represented in the third term and strongly depends on the ratio of the particle settling velocity to the fluid flow velocity. Interception and gravitational sedimentation collections increase the filter coefficient as  $d_p^{13/8}$  and  $d_p^2$ , respectively. Figure 4 is a plot of the clean bed filter coefficient at three flow velocities representing very fast, moderate, and slow groundwater flow. The curves have the characteristic minimums in the filter coefficient over the particle size range 1–5  $\mu\text{m}$  where there is a balance between Brownian diffusivity and collection by interception and sedimentation. The magnitude of the clean bed filter coefficients under these conditions predicts through (10) that very few particles could penetrate a distance of 1 m in an aquifer.

Experimental data on particle collection by clean media give filter coefficients that are within a factor of 2 of predicted filter coefficients from (11) when the experimental conditions have masked electrical double-layer forces [Yao *et al.*, 1971; Tien and Payatakes, 1979]. When an energy barrier exists between particles and the media surface, "collision efficiency factors" are inserted into the expressions for the individual particle capture mechanisms. These efficiency factors represent the fraction of particle-media collisions that result in attachment.

For small particles dominated by Brownian transport, particle collection in the presence of repulsive double-layer forces requires that individual particles possess sufficient energy to overcome the energy barrier and reach the primary minimum. The classical approach to this problem was developed by N. A. Fuchs [see Overbeek, 1952] for particle-particle collisions in the presence of interaction forces. The collision efficiency is approximately proportional to

$$\exp \left[ -\frac{(\phi_{dl} + \phi_a)_{\max}}{kT} \right] \quad (13)$$

where  $(\phi_{dl} + \phi_a)_{\max}$  is the maximum height of the energy barrier between colliding particles. The analysis of Brownian particle collection by filter media has followed a similar analysis and has arrived at a correction factor to the clean bed filter coefficient to account for double-layer repulsion that is approximately proportional to the expression in (13). The analysis was developed by Ruckenstein and Prieve [1973] and Spielman and Friedlander [1974] in slightly different ways, but both groups recognized the extreme sensitivity of (13) to surface potentials and ionic strength. For example, changing the ionic strength from  $10^{-1}$  to  $10^{-2}$  M for the 1- $\mu\text{m}$  particle depicted in Figure 3 changes the energy barrier from  $4 \times 10^{-12}$  to  $14 \times 10^{-12}$  erg, causing the collision efficiency to decrease by approximately  $e^{-250}$ , since  $kT = 4 \times 10^{-14}$  erg. Both Ruckenstein and Prieve [1973] and Spielman and Friedlander [1974] recognized the sensitivity to interaction parameters, especially when such interactions were greatest at particle-collector separations of a few nanometers where assumptions of spherical particles, smooth collectors, and a constant surface charge or constant surface potential were questionable. Spielman and Friedlander [1974] concluded that future advances would be

based on a semiempirical approach of experimental measurements correlated with system parameters as has found considerable success in quantifying aerosol particle filtration [see Friedlander, 1977]. Some experiments have been conducted for Brownian-dominated particles flowing through alumina fibers [Gregory and Wishart, 1980], but not for such particles in granular porous media. The work by Gregory and Wishart demonstrated the lack of agreement between theory and experiments when repulsive barriers are present.

Current research on small particle capture by more idealized collectors, such as flat plates and rotating disks, has been summarized by Adamczyk *et al.* [1983]. When double-layer forces are absent, theories and experimental data agree within 10–20%, but for any repulsive energy barrier between particles and collectors, predictions are very sensitive to surface potentials and the ionic strength. The approach adopted by Adamczyk *et al.* [1983] is to consider particle-collector interactions at separations of the order of a few nanometers where electrical double-layer forces are operating. The added effects they are considering in their analysis are surface roughness and surface heterogeneity in charge distribution. O'Melia [1986] also summarized the information on colloidal particle interactions in the presence of repulsive barriers and arrived at similar conclusions regarding the lack of quantitative agreement between experiments and mass transfer theory when attachment is unfavorable.

For larger particle capture by interception and gravitational sedimentation, quantitative predictions do not agree with experimental observations when double-layer forces are present. Probably the most complete experimental data set was collected by FitzPatrick and Spielman [1973], and they developed a semiempirical criterion for identifying conditions where double-layer forces were not important. Their experimental data suggested that for

$$\frac{2\kappa d_p N_\zeta N_{Ad}}{19.4 + 4N_{Gr}} \frac{e^{-\zeta}}{1 + e^{-\zeta}} < 1 \quad (14)$$

with

$$\zeta = \frac{\kappa d_p}{2} \left[ \frac{N_{Ad}}{19.4 + 4N_{Gr}} \right]^{1/2} \quad (15)$$

then electrostatic repulsion would not hinder particle collection. The dimensionless terms appearing in (14) include a zeta potential number:

$$N_\zeta = \frac{3e\zeta_p \zeta_m d_p}{4A} \quad (16)$$

an adhesion number:

$$N_{Ad} = \frac{4Ad_m^2}{9\pi\mu A_s U d_p^4} \quad (17)$$

and a gravity number:

$$N_{Gr} = \frac{(\rho_p - \rho_f)gd_m^2}{18\pi\mu A_s U} \quad (18)$$

the latter being oddly dependent on the media diameter rather than particle diameter. While the nondimensional criterion in (14) is compact, it hides insight into conditions for particle capture. For that reason, Figure 5 was developed from (14) for a 10- $\mu\text{m}$  particle flowing through 0.1-cm media at different ionic strengths and face velocities. Three regions of Figure 5 are designated: a central region of no collection where parti-



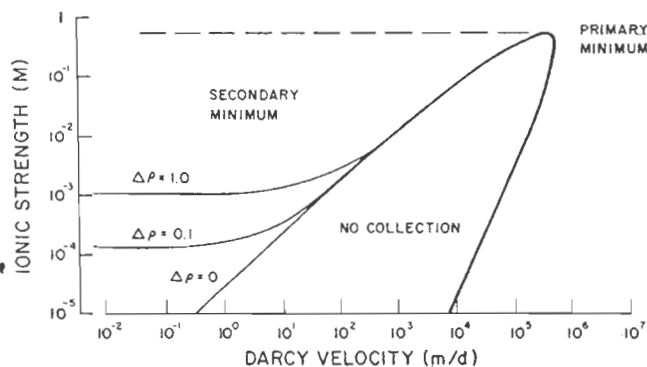


Fig. 5. Regions of particle capture by interception for a 10- $\mu$ m particle colliding with a 0.1-cm spherical media grain as a function of ionic strength, approach velocity, and particle density relative to fluid,  $\Delta\rho$ . Particle and media zeta potentials were assumed to be  $-30$  mV.

cles are predicted to not deposit; a region of collection in the primary minimum where either the ionic strength is sufficient to remove any double-layer repulsion ( $I > 0.5$  M), or where the fluid velocity is sufficient to push the particle over the energy barrier into the primary minimum; and a third region for lower ionic strengths and lower fluid flow velocities where particle capture in the secondary minimum is predicted. Sensitivity to particle density is also indicated in this region, which may be explained by the importance of sedimentation velocity in preventing collection in the secondary minimum. Spielman and Cukor [1973] showed that a particle trajectory analysis for interception collection alone ( $N_{Gr} = 0$ ) was in reasonable agreement with the empirical criterion in (14).

Quantitative application of (14) and Figure 5 should be approached with caution. First, the experimental data were collected over a range in flow velocities of 8.6 to 1300 m/d. Second, relatively few experiments were conducted in regions of double-layer repulsion. Third, there is an aspect to Figure 5 that appears counter to intuition. The separation between no collection and collection in the primary minimum indicates that with increasing ionic strength, where the energy barrier is decreasing, greater flow velocities are needed to avoid collection; the opposite is expected. Finally, Figure 5 gives a qualitative picture of the influence of fluid velocity on collection at a fixed ionic strength. At very low velocities, secondary minimum capture is predicted, and then with increasing velocity no collection is expected, until finally sufficient particle kinetic energy is available to overcome the energy barrier and primary minimum capture is possible. Flow velocities required for primary minimum capture exceed laminar flow conditions, casting further doubt on the quantitative applicability of the figure at higher flow velocities.

When double-layer forces are significant during particle-media collisions, experimental data on particle capture by interception and gravitational settling do not agree with available theories. Ives and Gregory [1966], FitzPatrick and Spielman [1973], and Jordan et al. [1974] observed smaller changes in filter performance than would be expected over a range in particle and media surface potentials and in solution ionic strength. As Spielman [1977, p. 317] stated, "... when electrical double-layer repulsion is significant, agreement between experiment and theory is so poor as to cast doubt upon the widely accepted view that van der Waals attraction and electrical double-layer repulsion alone adequately characterize surface interactions." The major problem in the theoretical analysis is that the energies of interaction are greatest where

the theory least applies, at very small particle-media separations. Again, as in collection of Brownian particles by porous media, an approach heavily based on experimental observations is suggested when double-layer forces are present.

3.3.4. *Models for particle removal during clogging.* If particle-media attachment and/or particle-particle attachments are energetically favorable, then deposited particles will accumulate within pore spaces. This deposit causes a decrease in media permeability as the porosity decreases, resulting in either lower fluid flow rates if the driving pressure is constant or higher hydraulic head losses at a constant flow rate. This coupling between particle accumulation and associated permeability reduction is the key to understanding particle and associated pollutant migration, accumulation, and possible sequestering within porous media.

For media surface potentials opposite in charge to the suspended particles, and when particle-particle attachment is not favorable, then little particle accumulation is expected, and less than monolayer coverage occurs on media surfaces. Heertjes and Lerk [1967] and Rajagopalan and Chu [1982] provide examples of submicrometer-sized particle collection on oppositely charged media. Rajagopalan and Chu model particle removal and migration by an adsorption reaction linear in particle concentration combined with an assumed desorption reaction linear in deposited particle concentration. The authors indicate that desorption is not likely to occur under conditions of attractive forces between particles and media, but desorption is assumed because it conveniently provides a maximum in particle adsorption and takes advantage of analytical results available from linear chromatography theory. Particle retention capacity is determined by a balance of charges between particles and media, corrected for excluded area effects, and the particle volume deposited is very small compared to the media pore volume. Under Rajagopalan and Chu's experimental conditions, a monolayer coverage of 0.3- $\mu$ m chromium hydroxide particles on 400- $\mu$ m glass media could reduce the pore volume by only 0.8%. Heertjes and Lerk observed no change in permeability as colloidal iron hydroxide deposited, indicating little flow restriction by accumulated solids. An adsorptive filtration model of Wnek et al. [1975] incorporates a charge balance for the filter media so that the electrostatic force between particles and media is continuously updated during filtration. Their model was able to reproduce Heertjes and Lerk's data.

When particle-particle attachment is favored, then substantial particle deposition can occur within pore spaces as particle aggregates grow out from the media surface. The analysis of particle deposit accumulation considers a balance on particle mass between what is suspended in pore fluid,  $C$ , and what is deposited,  $\sigma$ , mass per volume of bed. Assuming uniform flow velocity, negligible dispersion, and small local change in suspended solids concentration, the mass balance expression becomes [Herzig et al., 1970]

$$\frac{\partial \sigma}{\partial t} = -U \frac{\partial C}{\partial x} \quad (19)$$

For clean media, the particle concentration gradient for (19) can be substituted into the above equation and then solved for the deposit accumulation as a function of time and distance into the porous media:

$$\sigma(x, t) = UC_0 \lambda_0 e^{-\lambda_0 x} \quad (20)$$

valid only for  $\sigma \approx 0$ .



As particles accumulate, the clean bed filter coefficient  $\lambda_0$  no longer applies. One of the many empirical equations relating the filter coefficient during clogging to deposited particle volume has been used extensively by Ives [1970]:

$$\lambda = \lambda_0 \left[ 1 + \beta \frac{\sigma_v}{\varepsilon} \right]^y \left[ 1 - \frac{\sigma_v}{\varepsilon} \right]^z \left[ 1 - \frac{\sigma_v}{\sigma_{v,\max}} \right]^x \quad (21)$$

where  $\sigma_v$  is the volume of deposit per bed volume,  $\sigma_{v,\max}$  is the maximum deposit volume under the given conditions, and  $\beta$ ,  $x$ ,  $y$ , and  $z$  are positive empirical parameters evaluated from specific filtration data. This equation is based on three conceptual processes. The first bracketed term represents an increase in the filter coefficient as particles deposit caused by an increase in the surface area available for particle collection. The second bracketed term accounts for a decrease in particle filtration as pore spaces are filled and surface area available for deposition decreases. Finally, the third term causes particle collection to decrease as the fluid velocity within the pores increases. Calculating the volume of deposit,  $\sigma_v$ , from the mass of deposit requires an evaluation of deposit structure that is not readily available. Tien and Gimbel [1982] summarize other forms of corrections to clean bed filter coefficients to account for the effect of deposited particles. All the proposed equations contain adjustable parameters that must be evaluated from specific filtration data.

By analogy to the chromatographic separation of ions and molecules by adsorption to solids, models have been proposed for the migration of clogging fronts through porous media. The following relationship between concentration and deposit was derived by Ives [1963] and Herzig et al. [1970]:

$$\frac{C(x, t)}{C(x=0, t)} = \frac{\sigma(x, t)}{\sigma(x=0, t)} \quad (22)$$

Assuming a constant influent solids concentration,  $C(x=0, t) = C_0$ , and attainment of a maximum deposit of  $\sigma_{\max}$ , the clogging front has a predicted velocity of

$$U_c = U \frac{C_0}{\sigma_{\max}} \quad (23)$$

Experimental data that verify (22) and (23) are not readily available in the literature due to the difficulty of measuring deposited solids over time within a filter. Filtration data reported by Ives [1961], Cleasby [1969], Adin and Rebhun [1977], Letterman et al. [1979], Sandza [1981], and Rebhun et al. [1984] do not observe a steady state equilibrium deposit in clogging filters at a constant flow rate. Srinivasan [1981] measured the propagation of particle deposit within a sand column and found that a steady state deposit was reached in agreement with (22). Soo et al. [1986] have used (23) successfully in modeling oil droplet filtration by porous media, having tested their model with data collected at two different column lengths.

The other aspect of concern in porous media clogging is the reduction in permeability caused by deposited particles. For clean porous media of grain diameter  $d_m$ , the gradient in hydraulic head is accurately predicted by the Kozeny-Carman equation

$$i_0 = -\frac{dh}{dx} = \frac{6\nu U}{g} \frac{(1-p_0)^2}{p_0^3} \left( \frac{6}{d_m} \right)^2 \quad (24)$$

where  $h$  is the water head or fluid energy per unit weight and  $i_0$  represents the clean bed gradient. The final term in the

expression represents the square of the media surface area to volume ratio for a spherical grain. The coefficient of hydraulic conductivity,  $K$ , appearing in Darcy's law,

$$U = Ki_0 \quad (25)$$

can be expressed in terms of the fluid and media properties as

$$K = \frac{gd_m^2}{216\nu} \frac{p_0^3}{(1-p_0)^2} \quad (26)$$

or simplified using the media permeability  $k$ ,

$$k = \frac{d_m^2}{216} \frac{p_0^3}{(1-p_0)^2} \quad (27)$$

the latter term being a function only of the media.

When particles deposit within porous media, they act to both increase the media surface area to volume ratio and reduce the media porosity. Quantitative theories that predict changes in hydraulic gradients during particle collection have not been entirely successful. Herzig et al. [1970], Sakthivadivel et al. [1972], and Tien and Gimbel [1982] present summaries of proposed models for increased head loss caused by deposited particles. Many of the proposed formulas are of the form

$$i = i_0 \frac{1}{(1-\alpha\sigma)^m} \quad (28)$$

where  $\alpha$  and  $m$  are positive parameters. Equation (28) is frequently expanded into a power series in  $\alpha\sigma$ ,

$$i = i_0 \left( 1 + m\alpha\sigma + \frac{m(m+1)}{2} \alpha^2 \sigma^2 + \dots \right) \quad (29)$$

and when terms in  $\sigma^2$  and above are dropped, the hydraulic gradient increases linearly with particle deposition as is frequently, but not always, observed in filter columns. Kavanagh [1974] has termed the parameter combination  $m\alpha$  a compaction coefficient with measured values in the range 0.05–0.4 L/g, with larger media having smaller values at constant flow rates. Frequently, (28) and (29) are incorrectly applied to long (10–100 cm) filter columns where substantial depth variation in deposit occurs. The models leading to (28) are based on corrections to the Kozeny-Carman analysis by assuming particles deposit as a smooth coating that reduces the porosity and increases the media size. Adin and Rebhun [1977] and Rebhun et al. [1984] have observed that hydraulic gradients during filtration could be fit to the Shekhtman formula:

$$i = i_0 [1 - (\sigma/F)^{1/2}]^{-3} \quad (30)$$

where  $F$  is the theoretical filter capacity and is evaluated from filtration data. Sakthivadivel et al. [1972] concluded that the available models could each be fitted to experimental data, but the models were not predictive under new situations.

Filtration models that simultaneously account for the effect of deposited particles on particle capture and permeability reduction are few and incomplete. Adin and Rebhun [1974, 1977] modeled filtration with a kinetic equation incorporating expressions for deposition and detachment as was done by Rajagopalan and Chu [1982]. Adin and Rebhun did not attempt to model the final stage of filtration where the porous media reached an equilibrium in deposited particles. O'Melia and Ali [1978] and Tobiasson and O'Melia [1982] have developed a model for filter clogging based on particle capture



mechanisms on clean media and on previously captured particles that form dendritic patterns. The model could be fit to experimental data on particle removal and the increase in hydraulic gradient, but the model could not be verified with data not used for parameter calibration. Again, the final stage of filtration where a steady state deposit develops was not considered. Similar problems of model calibration were found by Tien *et al.* [1979] using experimental data collected by others. They also felt that better experimental data are needed for calibration and verification of models.

**3.3.5. Data on particle removal during clogging.** The general lack of experimental data on clogging filters is due to the experimental difficulty of determining suspended particle concentration, particle deposit, and hydraulic gradients in narrow layers within a filter over time. For clean media, filter behavior can be determined with relatively long columns, 10–100 cm in length, since initial homogeneity is assured. But when the particulate deposits are accumulating, much finer spatial resolution is necessary. Also, simultaneous measurement of particle concentration and specific deposit is rarely attempted within a filter. A number of studies using radioactive tracers or X ray absorbing materials have directly measured particle deposit within filters at 1-cm intervals [Stanley, 1955; Ives, 1961; Srinivasan, 1981; Sandza, 1981]. The spacing of manometer ports for determining hydraulic gradients and that of sampling ports for measuring suspended particle concentration were always much further apart. Alternatively, the specific deposit can be calculated by integrating the mass balance expression in (19), knowing the suspended particle concentration at discrete times and depths. Such an approach was adopted by Camp [1964], Cleasby [1969], Adin and Rebhun [1974, 1977], and Rebhun *et al.* [1984], where again sampling and manometer ports (if any) were spaced at various intervals. Experimental data from the literature can be examined to gain an insight into deposition and permeability reduction, avoiding where possible situations where particle-particle and particle-media attachments were dominated by chemical coagulants since coagulants tend to produce stronger aggregates and deposits than would be found in a natural environment where double-layer compression by electrolytes may be important [Adin and Rebhun, 1977].

In the analysis of operating water treatment plant filters, Hudson [1948] developed the concept of a floc strength index. Particulate suspensions were flowed through 61-cm-long columns containing media of different sizes, all at an approach velocity of 120 m/d, and the hydraulic gradients were reported when particles appeared in the column effluent (breakthrough). Hudson found that  $d_m^3 i_{bk}$  was nearly constant over a range of media sizes, where  $i_{bk}$  is the column hydraulic gradient at particle breakthrough. Particle breakthrough probably occurred when most of the column depth was at equilibrium. The actual value of the floc strength index depended on chemical conditions within the treatment plant and ranged from 0.2 mm<sup>3</sup> for weak floc to greater than 5 mm<sup>3</sup> for strong floc. Hudson did not try to expand the floc strength index to other flow velocities because 120 m/d was the conventional filter loading at that time, nor did he report on the mass of material retained within the filter columns at breakthrough.

Stanley [1955] measured the retardation of ferric hydroxide flocs within sand filters using radioactive iodine as a tracer. The data are presented as a penetration index that is the inverse of the bed-averaged deposit concentration. The profile

of retained solids within the clogging filter was not uniform with depth, and the retained floc concentration continuously increased near the filter surface as floc penetrated deeper into the filter. Changes in aqueous chemistry, influent floc size, and floc concentration were qualitatively observed to influence floc retention. Deposit accumulation was inversely proportional to approach velocity over the range of 59–310 m/d. Floc retention and head loss were very sensitive to media size. Measured particle deposits approached 6 g of solid per liter of bed with 0.42- to 0.59-mm sand media. The hydraulic gradient at 120 m/d was initially 0.5 but increased to 90 during clogging when measured over a 4-cm layer within the filter. Stanley observed that once solids deposited, they did not erode and greater accumulation was possible if the approach velocity was decreased during an experiment.

The soil formation process was simulated by Hunter and Alexander [1963] by passing clay suspensions in defined electrolyte solutions through silica sand columns. Clay suspensions at electrolyte concentrations less than the critical coagulation concentration resulted in slight reductions of media permeability, and an equilibrium in particle deposition was observed. A slightly greater permeability reduction was observed at  $1.2 \times 10^{-2} M$  compared to  $1.0 \times 10^{-2} M$ . At the critical coagulation concentration of  $1.6 \times 10^{-2} M$ , the permeability continued to decrease during the test without reaching an equilibrium value. The results at the low ionic strengths were qualitatively explained by the magnitude of the net attractive force in the secondary minimum which increases with increasing ionic strength as seen in Figure 3. Their experimental results also demonstrated considerable sensitivity of permeability reduction to temperature changes and again time of deposit. After equilibria in deposit and permeability were achieved at a low hydraulic gradient, increases in hydraulic gradient caused clay erosion and partial restoration in permeability. For example, at a hydraulic gradient of 1.5, equilibrium permeability was reduced by 20%, and a hydraulic gradient of 11 caused almost complete restoration in permeability. Their concepts of deposit yield strength and related equilibrium permeability reduction remain unchallenged and little tested.

Maroudas and Eisenklam [1965a, b] undertook studies of larger particle deposition in porous media where gravitational forces were felt to dominate over electrostatic forces. The media size was 2 mm with relatively large particles suspended in distilled water containing a wetting agent. Under constant flow conditions, equilibrium particle deposits were observed along with the existence of a critical approach velocity, above which no particle deposition occurs. Table 1 summarizes some of their results. Particle accumulation is, in general, inversely related to approach velocity, while for a given particulate suspension the hydraulic gradient slowly increases with increasing approach velocity. Increases in suspended particle size result in a stronger deposit such that the critical approach velocity increases. These data imply that particle deposition under constant flow conditions will result in an ultimate hydraulic gradient (permeability reduction) that is nearly independent of approach velocity. The authors noted that the flow was partially turbulent in the clean bed column but "laminar" in the column with particles accumulating.

The concept of a critical velocity developed by Maroudas and Eisenklam has been utilized by Kreissl *et al.* [1968] to determine optimum chemical coagulant additions for floc re-



TABLE 1. Particle Accumulation and Hydraulic Gradient Observed at Equilibrium in a Packed Bed of 2-mm Glass Spheres

Particle Size, $\mu\text{m}$	$U$ , m/d	$\sigma_{\text{max}}$ , percent	$i_{\text{max}}$
0-20	86	2.3	0.39
0-20	124	2.3	0.28
0-20	280	1.6	0.295
0-20	690	0.0	
65	220	7.6	4.55
65	860	4.3	6.45
65	3,000	2.8	10.1
65	8,600	0.0	15.
90	860	4.6	9.2
90	3,500	4.2	12.7
90	11,800	0.0	25.
125	790	5.6	9.2
125	2,900	5.4	14.2
125	12,400	0.0	30.

From Maroudas and Eisenklam [1965a, b].

tention within filters. Kreissl et al. recognized that the maximum particle deposition was the result of pore water velocities that prevent further deposition due to shear stresses. They then operated their clean filters near the pore water velocity desired during clogging to test if chemical additions achieved a floc strong enough for retention. For approach velocities of 120 m/d, hydraulic gradients reached 60 for 0.46-mm sand. B. Hudson's criterion these flocs are relatively strong with  $d_m^3 i_{bk} = 6 \text{ mm}^3$ . No particle deposition was observed at a flow rate of 400 m/d for these conditions. They did not report deposit accumulation within the filter column.

Cleasby [1969] provided a review of proposed filtration indexes that would provide a basis for determining conditions for both particle retention within a filter column and head loss minimization. A series of short filter columns is suggested for evaluating each particulate suspension and chemical addition rather than depending on an index calculated from particulate and media properties. For clay particles with no coagulant addition, the hydraulic gradient was observed to increase from 0.72 to 0.97 when approximately 2 g had accumulated per liter of filter bed at a flow velocity of 120 m/d. Hudson's floc strength index for the 0.7-mm sand was calculated to be 0.33, indicating rather weak aggregates as expected in the absence of chemical coagulants.

A number of researchers have noted that the material deposited within media pores is highly porous and does not have a constant composition during particle accumulation or following achievement of an equilibrium deposit. Eliassen [1941] observed that head loss continued to increase when no further deposition was observed in the top 4 cm of the filter media. Camp [1964] reanalyzed Eliassen's data and showed further that the filter coefficient corrections such as equation (21) were inadequate because filter coefficients at a given level of particle deposit depended on depth. Letterman's [1975] data on particle accumulation in filters show similar trends that can be qualitatively explained by deposit consolidation caused by aging and high fluid shear rates.

A completely qualitative study of filter clogging was undertaken by Payatakes et al. [1981] to investigate deposition and erosion processes within a filter. A two-dimensional model filter was used so that particle deposition and erosion could be observed. Uniformly sized latex particles were used with vary-

ing amounts of organic polyelectrolyte added to alter surface charge. A constant pressure drop across the filter was imposed, resulting in a gradual but unreported decline in flow rate during the experiments. Particle retention was observed to occur by selective pore plugging with flow redirected to open pores that remained open by high shear stresses. Particle deposits occasionally broke away from media surfaces, as clusters larger than influent particles, and were later captured by other media surfaces. This observation agrees with the reported tenfold increase in particle sizes leaving a clogged filter compared to the influent [Sandza, 1981]. Particle deposits were observed to be porous and partially permeable to fluid flow. An order of magnitude reduction in permeability was caused by only 10% of the void space being occupied by particle deposits.

In experiments designed to understand oil well productivity declines, Gruesbeck and Collins [1982] measured particle capture, permeability reduction, and deposit erosion within granular media and sandstone columns. For 0.275-mm sand a particulate suspension of 5- to 10- $\mu\text{m}$  glass beads was observed to occupy 7.2% of the bed volume at a flow rate of 140 m/d. The hydraulic gradient was 7.7, and Hudson's floc strength index of  $d_m^3 i_{bk} = 0.16$ , indicating relatively weak floc. For a flow rate of 520 m/d, only 1.6% of the bed volume was occupied by the particles, and the hydraulic gradient was 9.6 at equilibrium. These results qualitatively follow those of Maroudas and Eisenklam summarized in Table 1, although Gruesbeck and Collins did not determine fluid flow rates that prevented deposition. Well clogging was simulated by measuring particle release from a column at different flow velocities and aqueous compositions. Flow of a coagulating solution through a filter containing calcium carbonate particles did not erode the particles at an approach velocity of 190 m/d. At higher velocities the erosion rate was linear with velocity, indicating the existence of a critical erosion velocity. Particles deposited within the media pores were weakly bound and could be released by small mechanical disturbances.

Most of the data discussed thus far are for constant approach velocities, not constant driving pressure. Other data collected by Gruesbeck and Collins illustrate some of the major problems in conducting filtration experiments under constant pressure conditions. Two 20-cm-long columns were used, one with a mean sand diameter of 0.19 mm and an imposed hydraulic gradient of 91 and another with a mean diameter of 0.27 mm and an imposed gradient of 46. Following flow of the particulate suspensions through these columns, the smaller media column had a 90% reduction in permeability and nonuniform particle deposit over the column depth. The larger media column at a lower gradient achieved only a 20% reduction in permeability from its initial value and had a relatively uniform deposit accumulation over the column depth. Because of possible nonuniform particle accumulation and declining flow velocities during constant pressure filtration, subsequent mechanistic interpretation is difficult. In the case of Uebler and Swartzendruber [1982] and Swartzendruber and Uebler [1982], data and subsequent modeling of clay and sewage filtration by sands are dominated by declining flow rate which is not represented in their capture model. Mechanistic interpretation is hindered under constant pressure conditions for relatively long columns because only overall permeability reductions are reported and substantial variations in particle accumulation are likely [Goldenberg et al., 1983, 1984; Goldenberg, 1985].



The erosion of clay particles from soil, earthen structures, and estuarine sediments has received considerable attention that relates to aggregate erosion from porous media. A critical shear stress is required to erode clay deposits, and it depends on clay mineralogy, exchangeable cations, and the electrolyte concentration and composition [Arulanandan *et al.*, 1975]. At ionic concentrations below the critical coagulation concentration a clay deposit has a critical shear stress approaching zero, and any fluid motion could initiate erosion. The erosion rate is observed to be proportional to the shear stress, when it exceeds the critical shear stress  $\tau_c$ . Khilar *et al.* [1985] developed a criterion for erodability such that the hydraulic gradient required to initiate erosion is

$$i_c = 0.35 \frac{\tau_c}{\rho_f g} \left( \frac{p_0}{k} \right)^{1/2} \quad (31)$$

and since  $k \propto d_m^{-2}$ , the criterion becomes

$$i_c d_m \propto \tau \quad (32)$$

Although this criterion does not have the same dependency on media size as the floc strength index of Hudson, the criterion is in qualitative agreement on the factors included since critical shear stress is proportional to floc strength. Unlike Hudson, Khilar *et al.* did not present experimental data that checked their criterion for erosion.

#### 4. SUMMARY

The literature in a number of areas concerned with groundwater pollution, wastewater handling, petroleum extraction, hydrogeology, and waste isolation reveals the importance of particles in porous media, in terms of both transporting pollutants and reducing permeability. Information on particle migration and permeability reduction is usually available only from field studies where mechanisms are not easily identified, nor are characteristics of media and particles or aqueous chemistry well known. For bacteria and viruses in groundwater it is known that they may travel considerable distances, that they adsorb to solids including colloidal particles readily, and that aggregating bacteria may contribute to permeability reduction. Asbestos fibers are also known to be somewhat mobile in groundwater due to their colloidal size. The fact that hydrophobic compounds and radionuclides have been found to be more mobile in groundwaters than would be expected based on their adsorption potential suggests that some of the material to which they adsorb is mobile. This material may be clay particles or macromolecules such as humic substances, the migration of which is governed largely by aggregation and clogging phenomena. Furthermore, batch adsorption experiments which are often relied upon to predict adsorption potential of a compound may give misleading results if consideration is not given to the presence of a nonsettleable particulate phase.

Disposal and treatment of wastewater by surface spreading or aquifer recharge are greatly affected by the clogging phenomenon associated with suspended particulate matter and bacterial growth in the soil column or aquifer. These practices are highly dependent on maintenance of permeability to prevent such occurrences as in surface ponding. Thus mobility of the particulate matter is sometimes desirable. The fact that changes in aqueous chemistry may alter the mobility of particulate matter already residing in an aquifer is an important

factor considered in recharge operations and in the petroleum extraction industry. Remobilization of formation fines in sandstone reservoirs, for example, leads to reduced permeability, the formation, a situation which may or may not be desirable from the standpoint of petroleum recovery.

Immobilization of particles in porous media is sometimes the desired outcome. For example, the clogging properties of clay particles in particular are often relied on to seal canals, reservoirs, and waste disposal pits. Sand and gravel filters are designed to serve as barriers to eroded particulate matter from dams or soil that is being drained.

Finally, particle transport in porous media may be important in the realm of hydrogeology. The possible importance of subsurface particle migration in hydrogeological systems is now being recognized in terms of soil formation and organic carbon transport. Altered hydrogeologic systems such as in thermal energy storage, geothermal energy recovery, and waste isolation have recognized potential problems of particle transport and accumulation within porous media.

It is evident from the literature cited that particles are capable of substantial migration and of causing significant permeability reduction, depending on conditions at any given site. The ability to predict such migration becomes necessary if one is to assess a potential or actual groundwater pollution problem, engage in successful wastewater disposal practices that rely on maintaining permeability of aquifers, or develop successful waste isolation systems.

An extensive body of literature has developed within the filtration field that can be applied to understanding the transport of particles through porous media. The fluid mechanical particle capture by media surfaces is well known for various capture mechanisms, and experimental data are in reasonable agreement with predictions. Predictive capability is far less certain when electrostatic repulsive forces exist between particles and media and when media surfaces have become partially covered with retained particles. The available experimental data confirm the importance of parameters such as media size, particle size, media surface chemistry, particle surface chemistry, aqueous chemistry, and fluid flow rate. The deposit or aggregate strength and critical shear stress are of critical importance in understanding deposit accumulation, permeability reduction, and potential for erosion. Experience to date suggests that predictions of particle migration through porous media will be dependent on experimental data since quantitative predictions of colloidal forces during collisions and forces within deposited aggregates are unavailable.

Existing filtration data are not directly applicable to groundwater flow conditions. Groundwater flow velocities are usually less than 1 m/d compared to deep-bed porous media filters operated at greater than 100 m/d. The prediction that larger-sized particles moving at typical groundwater flow velocities can be captured independent of ionic strength (Figure 5) deserves investigation. Groundwater flow velocities are typically horizontal while filters are operated with vertical flow, and the distinction may be important for particle capture by settling. In filtration for water treatment, chemical coagulants have been used exclusively to promote particle-particle and particle-media attachments, a situation not encountered in natural waters. Furthermore, filtration experience has been with uniformly sized media, while natural aquifers have a wide media size distribution at a given point and considerable vertical and horizontal variability.



## 5. IMPLICATIONS

While an adequate mechanistic model of particle migration and accumulation within porous media is not presently available, the literature review and analysis of filtration theories and experimental data have some important implications in understanding fluid flow and pollutant transport in altered subsurface environments.

Particle mobilization or retention within groundwater aquifers can drastically alter media permeability. As was discussed, the alteration of aqueous solution composition can mobilize previously retained particles or cause particles to rearrange into a less permeable structures within media pores. Permeability alterations by orders of magnitude were caused by the presence of a relatively small percentage of swelling clays within the media. Such alterations have been reported in coastal aquifers and in laboratory-scale simulations. Other areas of potential flow field alteration would include brines or leachates released from disposal sites since their chemical composition is dramatically different from natural groundwater. Temperature changes are also known to alter subsurface flows because of mineral phase supersaturation and precipitation. Particle precipitation followed by attachment can drastically decrease media permeability and hinder underground heat storage and geothermal brine disposal.

Protection of groundwater supplies from contamination requires a mechanistic understanding of pollutant transport suitable for predictive modeling. Existing predictive models for groundwater contaminant transport are based on the concept of partitioning the pollutant between a mobile aqueous phase and an immobile, adsorbed phase [Gillham and Cherry, 1982]. One of the simpler models assumes local equilibrium and linear, reversible adsorption isotherms that are characterized by a distribution coefficient  $K_d$ . Neglecting dispersion, the contaminant migration velocity through porous media,  $U_a$ , is retarded compared to the fluid velocity according to

$$U_a = \frac{U}{1 + (\rho_m K_d / \rho_0)} \quad (33)$$

where  $\rho_m$  is the bulk media density. Compounds with greater distribution coefficients are predicted to have a greater reduction in migration velocity. Reardon [1981] and Valocchi [1984], however, point out that distribution coefficients depend on local solution chemistry and that nonequilibrium conditions are likely. A number of laboratory and field examples were discussed earlier that found that batch determined  $K_d$  values did not accurately predict observations. This may be due, in part, to the fact that some adsorptive pollutants are associated with colloidal particles present either in the inflow or within the porous media. Transport of pollutants adsorbed to mobile particles would be dominated by particle removal mechanisms that are not related to linear chromatography theory as represented in (33).

For pollutants associated with initially suspended particles, particle capture may result in pollutant sequestering. Particle capture and subsequent permeability reduction would cause flow field alteration such that fluid flow would decrease in the region of particle and contaminant accumulation. The low permeability zone then acts as a trap for the pollutant since the advective velocity is reduced and leaching is hindered.

Other problems exist in predicting pollutant migration if

one is not aware of the particulate component. For example, the use of glass wool or other filters in soil column experiments to filter the column influent and effluent may invalidate migration studies because particle-associated contaminants are being retained by artificial media rather than the soil column of interest. Similarly, soil column repacking to eliminate macropores or secondary porosity can significantly decrease bacterial migration and possibly other particles over what might occur under field conditions.

Finally, the presence of a particulate component may complicate the monitoring of subsurface contaminant migration. Although the purpose of well development is to remove fines in the vicinity of the well casing, monitoring sometimes involves sample filtration prior to chemical analysis to insure that fines are not present in the sample. This practice biases reported contaminant levels to those forms which pass through the filter. On the other hand, the amount and origin of suspended matter in the well vicinity likely differ from those in the undisturbed aquifer as a result of well development, making it impossible to obtain representative samples of the naturally occurring particulate phase.

Particle transport in porous media is an important process in the hydrogeological environment as well as in engineered systems. Predictions of particle retention and permeability reduction are dependent so far on pilot plant experiments or site-specific field studies. These may be useful if one is designing a filter or using a specific aquifer recharge site, but not so if one is concerned with predicting particle migration in natural aquifers where a more fundamental understanding of mechanisms is required. Theoretical developments and pertinent experimental data are necessary to assess conditions for particle retention, aggregate formation, permeability reduction, and the potential for deposit erosion by changes in flow or solution chemistry.

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